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Uranium chemistry and pinning centers in high temperature superconductor

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Abstract

A study has been made of compounds formed when up to 1% uranium oxide is added to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Y123), prior to texturing. Initially, the study was to create pinning centers by addition of UO_4 , followed by neutron fission of some of the ^{235}U component. It was found that, prior to fission, the chemical reaction of U provides sufficient pinning centers to approximately double J_c . The U forms in deposits about 300 nm in diameter. The number of such deposits is proportional to the mass of U. TEM and XRD studies identify the compound as $(\text{U}_{0.6}\text{Pt}_{0.4})\text{YBa}_2\text{O}_6$, a double perovskite. Neither T_c nor creep vary with %U. The uranium compound has also been produced outside of Y123. The behavior of uranium in high temperature superconductor (HTS) is thus of interest not only for introducing pinning centers by neutron fission of U but also as an effective chemical method to increase J_c . © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Chemical pinning center; Critical current density; Magnet of superconducting material; Flux pinning

1. Introduction

Pinning centers in high temperature superconductor (HTS) have been created by means of chemical, mechanical and radiation effects. A very promising radiation method for textured $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Y123) utilizes the fission of uranium (U) by thermal neutrons [1–3]. Y123 powder is mixed with UO_4 , tex-

tured,¹ and then irradiated with thermal neutrons. This U/n method has been shown to make possible trapped fields, in the critical state, of over $B_t = 2$ T in a single, textured [5] 2.0 cm diameter grain [2], and $J_c \sim 300,000$ A/cm², at 0.25 T applied field, both at 77 K [3]. Depending on applied field, H_A , and temperature, T , the method increases J_c by factors of 15–40 [3].

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¹ Uranium in *sintered* Y123, followed by neutron irradiation was investigated by Luborsky et al. [4]. The intergrain J_c values obtained by such a method for large objects are tiny compared to either the U/n or U-Chem methods.

One question, initially, regarding the U/n method was whether the chemical behavior of uranium in the HTS would spoil the properties and the texturing of the superconductor. We report here on the addition of U to Y123. In this study, we evaluate the textured material, including U but not irradiated. We find that chemical effects of U, without irradiation, *improve* textured Y123. Because of the magnitude of the increase in J_c , we consider this ‘U-Chem’ process, without irradiation, to be interesting in its own right, as well as for its role as a precursor to neutron irradiation.

2. Experimental method and results

2.1. Uniformity of samples

It is necessary when varying the %U, that all other variables effecting J_c be kept constant. The amount of U is fixed once the sample is textured, and as a result many textured samples must be used to study effects of changing variables. In early studies of use of the U/n method to enhance J_c [1] there appeared to be an enhancement of J_c and B_t before irradiation. However, samples with J_c reproducible to 15% were not available at that time. Even changes of chemical batches from a single supplier of Y123 or Y211 powders change J_c and B_t significantly. Sample uniformity was improved as we sought higher trapped fields [2,6,7] culminating in a trapped field of 10.1 T [2], and a sample uniformity of $\Delta B_t \sim \pm 15\%$. The present experiments were then done. The chemical batch used was not the best material, but was received in large enough supply to provide samples for the entire experiment.

2.2. Processing

Textured samples of Y123, 2 cm diameter \times 0.8 cm thick, were used, the size used for prior work on trapped field magnets. To the Y123 powder, plus 60% (atomic) excess Yttrium, plus 0.5% Pt (wt.), we add $X\%$ U (wt.). The excess Y reduces the size of Y211 deposits remaining after texturing, enabling larger sample radii [8], and resulting in higher J_c [9]. The higher J_c results from the small non-superconducting Y211 deposits, or the Y211–Y123 interface,

acting as pinning centers [9]. The Pt addition elongates the small Y211 deposits [10].

The powders are ball milled, melt textured [5] using a top seed of $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [6], and then oxygenated.

It should be stressed that texturing was done using the same temperature profile which was used in the absence of U.

2.3. Characterization of superconductor

Trapped field was tested by field cooling, in liquid nitrogen, in a 2.4 T electromagnet, with field parallel to the c -axis. After this, the applied field was reduced to zero. The c -axis component of maximum trapped field was then measured with an axial direction Hall probe at 0.6 mm from the surface. $B(x,y)$ in the a,b plane was measured using an automated x,y positioning stage, with the Hall probe 1 mm from the circular (a,b plane) surface.

We introduce the variable

$$R_M(x) \equiv B_t(X\% \text{ U}) / B_t(0\% \text{ U}),$$

where B_t is the peak trapped field of the sample in the critical state. The values of R_M , at liquid nitrogen temperature, vs. X are shown in Fig. 1. Each point of Fig. 1 represents the average R_M of four samples. The trapped field is increased significantly owing to the presence of U. The highest trapped field increase measured was $\Delta R_M = 65\%$, for 0.8% U (wt.). Note that B_t for the point at 1.0% U (wt.) was not measured because the samples produced with 1% U did not have single grain structure.

Other tests of sample quality were done. Field plots of $B_t(x,y)$, on the circular sample surface were compared to theory for single grain flux trapping [11,12] and found to give an excellent quantitative fit. An isometric view of $B_t(x,y)$ is given in Fig. 2.

T_c was measured by the D.C. magnetization method, and found to be constant, an indication that the quality of the Y123 matrix is not worsened by the UO_4 addition (see Fig. 3).

Creep was measured via loss of trapped field over 120 min. The creep from 10 to 100 min was parametrized as

$$B_t(t_2) = B_t(t_1)(1 - \beta \log t_2/t_1). \quad (1)$$

The fit value of β is used to represent the creep. Fig. 4 shows that β vs. %U (wt.) is essentially constant

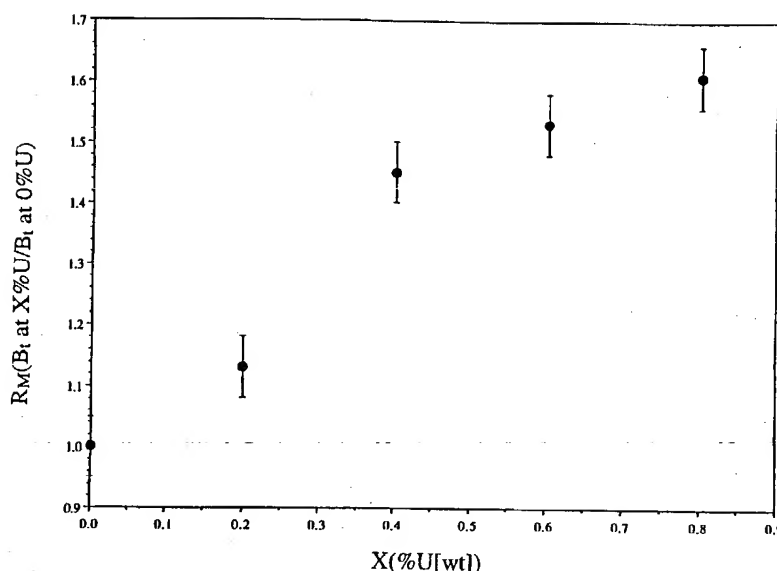


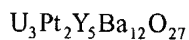
Fig. 1. Data showing R_M vs. %U (wt.), where $R_M \equiv B_t(X\%U)/B_t(0\%U) = J_c(X\%U)/J_c(0\%U)$.

as is the case with the chemical method involving addition of Y_2BaCuO_5 to Y123 [9]. In comparison, increases in J_c accomplished with irradiations by protons [6], neutrons, or fission fragments [3] are accompanied by an increased rate of creep.

2.4. Microstructure

SEM studies were done of the microstructure of the U-doped Y123. These showed that profuse small deposits, containing U, are formed (see Fig. 5). The

U compound is found to form in Y123, but not in Y211. TEM microprobe studies of the deposits containing U indicated the approximate atomic weighting of the U deposits is



Compound 1

Essentially no U was found to substitute into the Y123 matrix, and no Cu was found in the U deposits.

Fig. 6 shows a TEM study of a typical deposit of compound 1 (C-1). The deposits are quasi-spherical,

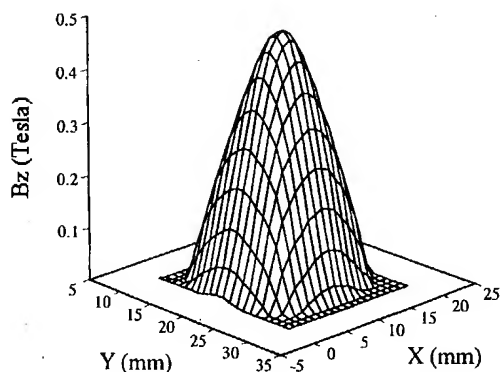


Fig. 2. Trapped field of a single grain of Y123, 2 cm diameter \times 0.8 cm thick. Analysis of curve shapes indicate a single grain is present. Mass of U is 0.8% (wt.).

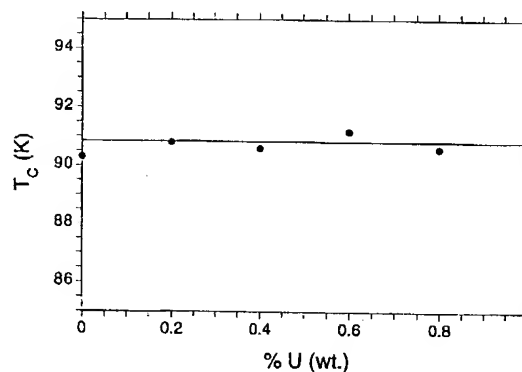


Fig. 3. Data showing T_c in textured Y123 vs. %U (wt.) added.

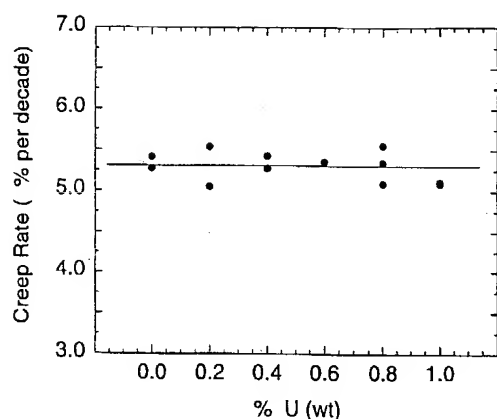


Fig. 4. Data showing creep parameter, β , vs. %U (wt.), in textured Y123.

and appear in a narrow spectrum of sizes around a diameter of ~ 300 nm. They appear detached from the Y123 matrix, which is consistent with the null effect of U upon T_c and β .

The size and shape of the Y211 and the C-1 deposits do not change with the addition of U. The number density, n , of C-1 deposits increases approximately linearly with the mass of added U, which we call X , i.e., $n \propto X$. Consequently, the separation of deposits is $\delta \propto 1/X^{1/3}$. For example, for 0.6% UO_4 (wt.). The average planer spacing observed via SEM was 2.6 μm .

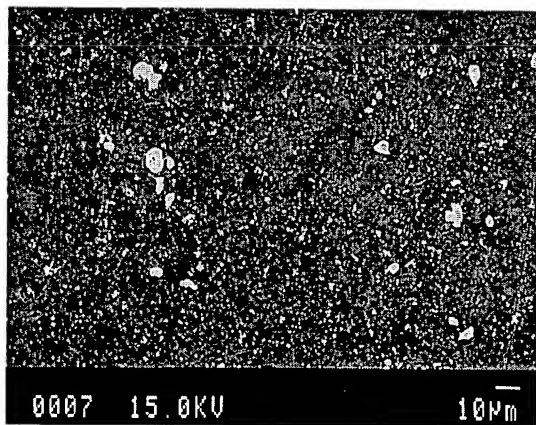


Fig. 5. SEM backscattered electron image of textured Y123 + 60% Y (atomic) + 0.5% Pt (wt.) + 0.6% U (wt.). Small deposits are $(\text{U}_{0.6}\text{Pt}_{0.4})\text{YBa}_2\text{O}_6$. Large deposits are $\text{PtBa}_4\text{Cu}_2\text{O}_7$.

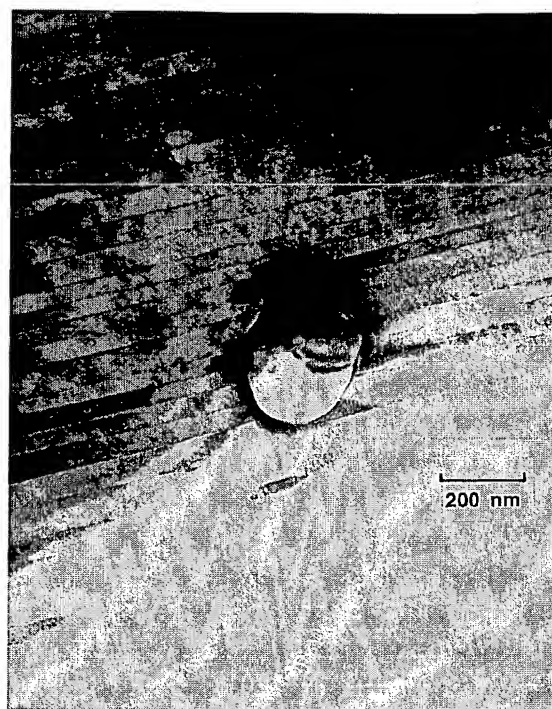


Fig. 6. TEM photomicrograph of a typical deposit containing U, in textured Y123. The compound containing U is $(\text{U}_{0.6}\text{Pt}_{0.4})\text{YBa}_2\text{O}_6$.

On the other hand, platinum deposits not containing U are large, $\sim 1\text{--}10$ μm , and irregular. The composition of the Pt deposits was found to be



The Pt deposits of C-2 were found to be numerous for samples with low X . As X was increased, fewer of these Pt deposits are seen. At about $X = 1\%$ U (wt.), no Pt deposits are seen. Thus, as X is increased, the Pt appears to be used up in a preferential reaction to form C-1.

Earlier experiments, without added Pt, also showed U in small deposits [1]. The composition of this non-platinum compound was



In later work, 0.5% Pt is used to achieve large sample sizes [2]. In Y123 with both U and Pt added, when $X < 1\%$ (wt.), C-1 is formed. When $X > 1\%$ (wt.) the Pt has been essentially used up by C-1 and then C-3 forms. The work described below was done with $X < 1\%$ UO_4 (wt.), and hence produced C-1.

Studies of the region $X > 1\%$, and the detailed structure of C-3, are in progress.

2.5. Investigation of the UPtYBaO compound

A set of experiments were undertaken to produce C-1 outside Y123, in order to study chemical substitution, elongation, and use for direct insertion of U into Y123, as well as into other HTS. If C-1 is stable during texturing, admixing C-1 in place of UO_4 has the advantage of maintaining the desired stoichiometry of Y123.

A precursor of UO_4 , Pt, Y_2O_3 and BaCO_3 was mixed in the ratio $\text{U}:\text{Pt}:\text{Y}:\text{Ba} = 3:2:5:12$, as found in the TEM-microprobe studies. Samples were reacted at temperatures between 925 and 1225°C for up to 150 h. No visible reaction took place in these samples, and SEM analysis showed that no compound was formed which contained all five elements in the ratio found previously. Thus a stoichiometric mix of

the elements required for C-1 alone does not produce C-1. It appeared that some element in Y123 acted as a catalyst.

A second set of samples was therefore processed in contact with various compounds of the Y–Ba–Cu–O system, to see if one of them acts as a catalyst. Samples of the UPtYBaO precursor were placed on pellets of either Y123, Y_2O_3 , Y211, CuO, BaCO_3 , Cu foil, or a mixture of BaCO_3/CuO . CuO mixed into the UPtYBaO precursor sample was also tried. The samples were then processed with the standard melt-texturing profile for YBCO.

Samples processed on supports of Y211 or Y_2O_3 did not react visibly. Samples processed with CuO or Cu foil resulted in a loose dark yellow material, with millimeter-sized inclusions of a hard phase with the appearance of silver. This phase also accumulated on the surfaces of the samples. SEM studies showed that this phase consisted of CuO, Ba_3UO_6 and the C-1 compound. The loose yellow material was C-1.

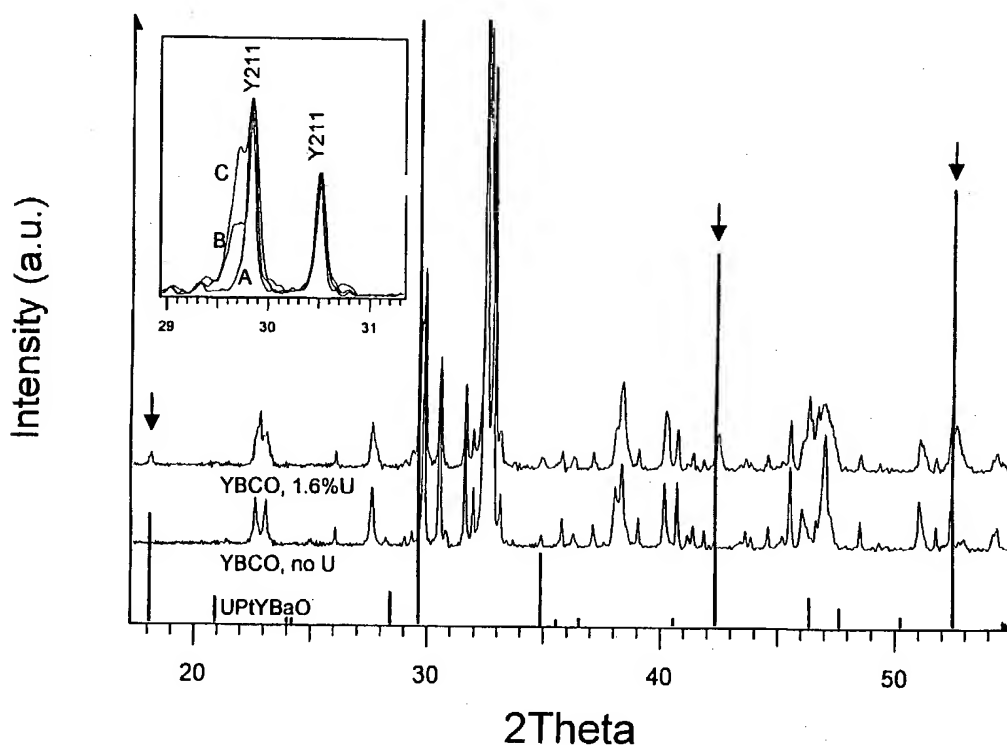


Fig. 7. XRD patterns of: (top) textured Y123 + 1.6% U; (middle) Y123 without U; and (bottom) marker bars for EC-1. Peaks of EC-1 in U-doped Y123 rise above background at the positions marked with arrows. The insert shows a blow-up of one of the increases of counts with U addition, the (220) peak of EC-1 (A: no U; B: 0.8% U; C: 1.6% U) while the peaks of Y211 remain unchanged.

Samples processed on Y123 or BaCO_3/CuO also contained C-1, however intermixed with many other compounds. Samples processed on BaCO_3 reacted partially to a light yellow material, which contained a compound with all five elements of C-1, but not in the ratio found in C-1.

C-1 is indeed a compound (not just a mixture of compounds) since the atomic ratios in different grains are always the same. Cu was found to be needed to produce the compound at temperatures below 1200°C . The best separation between the UPtYBaO compound and other phases is achieved by processing the precursor on a CuO base or on Cu foil.

We will refer to C-1 made externally to Y123 as EC-1.

The EC-1 from samples sintered on CuO bases was separated *mechanically* from the other phases and analyzed by powder X-ray diffraction (Siemens D5000). The resulting diffraction pattern was indexed with the Siemens WIN-Metric program. The data fit an fcc symmetry with a lattice constant of 8.53 \AA . Two peaks, not indexed, of varying intensity in different samples can be attributed to CuO impurities. No other impurities were observed with XRD.

A refinement fit showed that the C-1 compound is a double perovskite [13], of the form AAB_2O_6 , with the chemical formula



with lattice constant $a = 8.53396 \text{ \AA}$, where one site is completely occupied by Y, and the other by a mixture of Pt and U. This is a result consistent with atomic weighting in the formula for C-1.

Further XRD was performed on three samples of Y123 to confirm that the U-deposits in YBCO consist of the EC-1 compound described above. Sample A was doped with 0.5% Pt and no U, sample B with 0.5% Pt and 0.8% U, and sample C was doped with 1.0% Pt and 1.6% U. In the resulting diffraction patterns, the count rate of samples B and C compared to sample A, increased at angles corresponding to the peaks of EC-1. This increase could be observed at nine individual angles, four of them sufficiently separated from Y123 or Y211 peaks to exclude errors from angle or intensity variations due to oxidation status, etc. (see Fig. 7). Also, the increase in count rate of sample C was about twice the

Table 1
Observed and calculated peak position, d_{obs} and d_{calc} , of the XRD spectrum of $(\text{U}_{0.6}\text{Pt}_{0.4})\text{YBa}_2\text{O}_6$

$d_{\text{obs}} (\text{\AA})$	$d_{\text{calc}} (\text{\AA})$	h	k	l	Intensity (%)
4.9313	4.9244	1	1	1	8.3
4.2674	4.2647	2	0	0	2.0
3.0171	3.0156	2	2	0	100
2.5725	2.5717	3	1	1	5.5
2.1329	2.1323	4	0	0	28.4
1.9572	1.9568	3	3	1	2.2
1.9073	1.9072	4	2	0	1.4
1.7414	1.7410	4	2	2	33.5
1.6411	1.6415	3	3	3	2.2
1.5078	1.5078	4	4	0	12.2
1.4414	1.4417	5	3	1	1.8
1.3486	1.3486	6	2	0	10.5
1.2313	1.2311	4	4	4	2.7
1.1398	1.1398	6	4	2	9.3
1.0663	1.0662	8	0	0	1.0
1.0054	1.0052	8	2	2	4.1
0.9534	0.9536	8	4	0	2.7

increase of sample B, as expected from the amount of uranium added. Table 1 shows the XRD results of EC-1.

3. Summary and discussion

The addition of UO_4 to Y123 + Pt followed by texturing and neutron irradiation has been shown to lead to the highest values of J_c seen to date in textured material [3,14]. Prior to irradiation, it is observed that the addition of UO_4 increases J_c , albeit by a smaller amount than post-irradiation. However, the magnitude of the increase in J_c , without subsequent irradiation, is large enough to make this U-Chem process interesting in its own right, even more so because the product has no significant radioactivity.

UO_4 is added to the normal mix for textured Y123 (Y123 + 60% excess Y [atomic] + 0.5% Pt [wt.]), followed by texturing [5]. The temperature profile for texturing U-Chem Y123 was unchanged from the one ordinarily used. C-1 forms for $0 \leq X \leq 1\%$ U (wt.). For this range of X , trapped field was observed to increase 65%, from 0.36 to 0.60 T.

J_c can be deduced directly from trapped field plots, $B(x,y)$ [11,12]. Also, J_c calculated in this

way agrees within 10% with measurements made by VSM or SQUID [11,12].

We have defined $R_M = B_i(X\% \text{ U})/B_i(0\% \text{ U})$. Because geometries of the samples are constant, $R_M = B_i(X\%)/B_i(0\%) = J_c(X\%)/J_c(0\%)$. Thus, R_M also gives the ratio of J_c with $X\%$ U to J_c with 0% U. However, as shown in Fig. 1, B_i increases with X . As a result R_M compares, e.g., J_c at 0.36 T (0% U), to J_c at 0.6 T (0.8% U). The usual procedure for measuring changes of J_c is to compare J_c values at a constant magnetic field. Because magnetic field generally lowers J_c , R_M underestimates the improvement ratio of J_c , which we will call R_J . We correct for this effect by using measured values for the dependence of J_c on applied field [14] in U/n melt textured Y123. We find that the increase in $J_c(0.8\% \text{ U})/J_c(0.0\% \text{ U}) = 1.90$. We conclude that doping Y123 with U, and not changing the texturing process in any other way, can increase J_c by at least 90%, or about 11% per 0.1% U (wt.).

The increase of J_c associated with addition of UO_4 appears to be due to an increase in the number of pinning centers. The U deposits are found to be relatively small (~ 300 nm diameter) and composed of $(\text{U}_{0.6}\text{Pt}_{0.4})\text{YBa}_2\text{O}_6$, a face centered cubic double perovskite with $a = 8.53396$ Å. Experimental evidence suggests that at $X \sim 1.0\%$ U (wt.), the 0.5% Pt (wt.) is totally consumed in the U deposits, and for $X > 1.0\%$ the U forms $(\text{U}_{0.4}\text{Y}_{0.6})\text{BaO}_3$.

Using the structure of C-1 to calculate [13] the density of C-1 indicates $\rho_{\text{C-1}} \sim 6.8$ g/cm³.

Experiments in progress should determine the upper limits of R_J and R_M which are achievable in this process (i.e., how much U, Pt, or C-1 can be added to Y123 before the HTS is spoiled). The range $0 \leq X \leq 3\%$ is being explored. Other experiments in progress are intended to form $(\text{U}_{0.6}\text{Pt}_{0.4})(\text{RE})\text{Ba}_2\text{O}_6$ for RE = Nd or Sm, which may also be useful in other HTS systems. Additional experiments test substitution of elements.

Because no neutron irradiation, or fission, is utilized, commonly available depleted U can be used (99.6% U238). Because the processing is unchanged in the U-Chem method, the only added cost, to improve textured Y123 by the U-Chem method, is for inexpensive depleted U ($\sim \$4/\text{g}$), e.g., for a 15 g trapped field magnet, with 1% U (wt.), 0.15 g of U is used at a cost of about 60 cents. Thus the U-Chem

method represents a way to improve bulk Y123 (e.g., trapped field magnets) without use of radiation.

In the U/n method, the resulting radioactivity is small but not negligible. In the U-Chem method, using depleted uranium, measurements of the radioactivity of 0.8% U (wt.) in 15 g samples of Y123 show that the radiation, at contact, is indistinguishable from the omni-present cosmic ray background radiation in Houston, TX. Radioactivity is an emotional issue in our society, and this may auger for preferred use of the U-Chem method vs. the U/n method, despite its much lower gain.

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